Chloride ions enhance furfural formation from D-xylose in dilute aqueous acidic solutions

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Furfural production through traditional processes is accompanied by acidic waste stream production and high energy consumption. Modern furfural production process concepts will have to consider environmental concerns and energy requirements besides economics, moreover will have to be integrated within widened biorefinery concepts. In this paper, some particular aspects of the chemistry of D-xylose reaction to furfural are addressed, with the aim to clarify the reaction mechanism leading to furfural and to define new green catalytic pathways for its production. Specifically, reducing the use of mineral acids is addressed by the introduction of alternative catalysts. In this sense, chloride salts were tested in dilute acidic solutions at temperatures between 170 and 200 °C. Results indicate that the Cl^- ions promote the formation of the 1,2-enediol from the acyclic form of xylose, and thus the subsequent acid catalyzed dehydration to furfural. For this reason the presence of Cl^- ions led to significant improvements with respect to the H_2SO_4 case. The addition of NaCl to a 50 mM HCl aqueous solution gave 90% selectivity to furfural. Among the salts tested $FeCl_3$ showed very interesting preliminary results, producing exceptionally high xylose reaction rates.

Introduction

Furfural is a readily accessible chemical from lignocellulosic biomass, being produced industrially since 1921. It has enormous potential as a starting material, both in the chemical industry and for liquid fuel production. On the other hand, environmental concerns combined with energy and waste streams disposal costs, are among the main reasons why furfural production in EU and USA has been strongly hampered in the last few decades. The severity required in order to obtain good furfural yields, both in terms of mineral acids concentration and process temperatures, is not practical with current environmental constraints and energy costs. Novel green process concepts are needed in order to minimize the carbon footprint and waste streams related to furfural production. In this way, the great potential of furfural as a biomass derived intermediate in the chemical and fuel industries could be unlocked to the disadvantage of oil derivatives.[1] To achieve this, a deeper comprehension of the chemistry of pentoses is needed, as well as the establishment of new catalytic pathways for their conversion into furfural.

Furfural can be gained relatively easily from nearly all kinds of lignocellulosic biomass. For this reason, in the past, various standard methods based on furfural production were established for the estimation of pentosans content of plant material.[2] Among others, one standard method first described in 1938[3] is commonly accepted,[1] where 100% of the initial pentosans can be recovered as furfural when the raw material is distilled atmospherically in a 12 wt% HCl solution saturated with NaCl. Evidently, such reaction conditions are prohibitive for any industrial scale application due to the high chemical utilization. Nevertheless, a deeper understanding of the reaction mechanism taking place under those conditions is necessary in order to approach the same yields under significantly milder conditions. The acid choice was simple, since it is known from literature that different acids catalyze differently the dehydration of pentoses into furfural,[2] and among strong acids HCl is reported to be the preferable choice.[1,2] Such observation suggests that the mechanism of furfural formation goes beyond the specific acid catalysis. Also very important is the role played by NaCl, which besides the salting-out effect enhancing the separation of furfural during distillation, was reported to increase sugars reaction rate. Such effect was thought to be the combined result of the higher boiling temperature and of the increased activity coefficient of the acid.[2,4]

More recently it was shown that the addition of KCl, NaCl, $CaCl_2$, $MgCl_2$ or $FeCl_3$ to pure water increased the reaction rate of both xylose and xylotriose at 180 °C. This effect was more pronounced for xylotriose than for xylose.[5] Similar results were reported in recent works when treating corn stover with diluted inorganic salts.[6,7] A peculiar catalytic effect of $FeCl_3$ on hemicellulose hydrolysis was also evidenced in these works, and $FeCl_3$ in water was shown to be significantly more effective than a strong acid solution of the same pH. In particular it was shown[7] that Fe^{3+} and Cl^- ions are both responsible for this effect. Gravitis *et al.*[8] reported the metal cations to catalyze the reaction of biomass derived carbohydrates to furfural proportionally to their ionization potential, mentioning an increasing effectiveness respectively for K^+, Na^+, Ca^{2+}, Mg^{2+}, Fe^{3+}.

Furthermore metal salts, and especially metal chlorides, have been shown to have significant effects in microwave aided hydrolysis of chitosan,[9] the hydrolysis of ethers and amines in

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near and supercritical water,[10] but also on hemicellulose and cellulose hydrolysis both in solid state[11,12] and in dilute aqueous solution.[5,6,7] Some metal chlorides have also been shown to affect the dehydration of glucose and fructose to HMF in ionic liquids.[13]

This paper addresses the use of different chloride salts for furfural production, evaluating the role of the different electrolytes in solution in terms of xylose rate of reaction and furfural selectivity and yield, with the aim of exploring new catalytic pathways leading to high furfural yields with a reduced mineral acid usage.

Results and discussion

Fig. 1 shows the results of xylose dehydration in dilute aqueous acid solutions with the addition of different amounts of NaCl. The reaction rate of xylose in two equimolar solutions of HCl and H_2SO_4 at 200 °C does not show a significant deviation, nevertheless furfural yield is significantly higher in the former case with respect to the latter. The second dissociation constant of H_2SO_4 is known to decrease markedly with temperature,[14,15] to such an extent that H_2SO_4 can be considered with very good approximation to be monoprotic at 200 °C ($pK_{a2} \simeq 4$), and consequently the H^+ concentration of two equimolar solutions of HCl and H_2SO_4 can be assumed to be equal at those conditions. The different results in terms of furfural yield can thus be ascribed to the presence of different anions in solution, in particular Cl^- having a more beneficial effect than HSO_4^-.

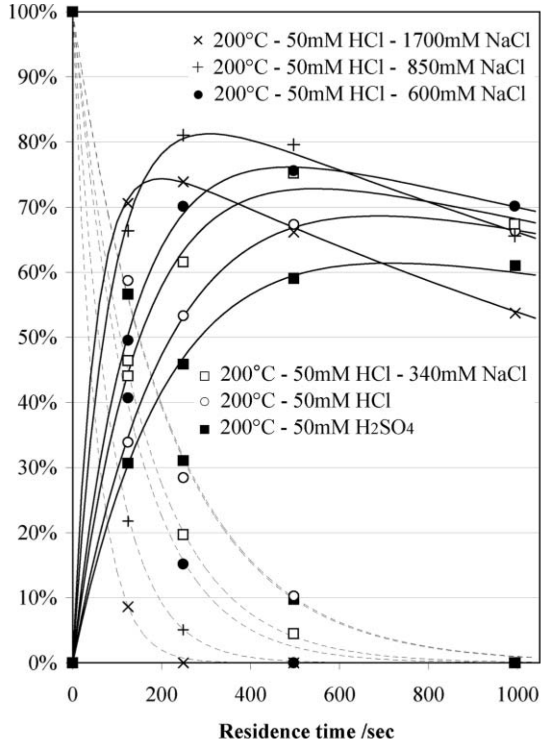

Fig. 1 Effect of NaCl addition on xylose conversion and furfural yield. Xylose (dotted line) and furfural concentration (solid line) as from eqn (2) after fitting to the experimental results.

In the presence of increasing amounts of NaCl in dilute aqueous HCl a clear increase in xylose reaction rate is immediately evident and surprisingly higher furfural yields are achieved, see Fig. 1. Thus NaCl is confirmed[4] to affect xylose reaction rate already at relatively low concentrations in acidic solutions, although, contrary to what was believed before,[2,4] this effect can neither be ascribed to the increased activity of the acid, nor to the increased boiling temperature or the salting-out effect. From the Debye-Hückel theory the ions activity coefficient γ can be related to the ionic strength I in dilute solutions according to the equation $\log_{10}\gamma_i = -Az_i^2 I^{1/2}$, in which the expression z is the ion charge and A is a constant dependent on temperature, density and dielectric constant of the solvent.[16] Thus, under these conditions of dilution, increasing the salt concentration leads to a decrease of the ions activities, and consequently to a decreased acid activity. Furthermore, the reaction is carried out at constant and controlled temperature in liquid solution without any separation by steam stripping, thus boiling point raise or salting-out effect do not play any role in this case.

In a previous work[17] where H_2SO_4 was used as catalyst for the production of furfural from xylose in the same range of conditions used in this work, increasing the temperature led to negligible variations in terms of furfural selectivity and yield. Contrary to this result, in Fig. 2 it is shown how a significant increase of furfural yield can be obtained raising the temperature from 170 to 190 °C when dilute HCl is used instead of H_2SO_4.

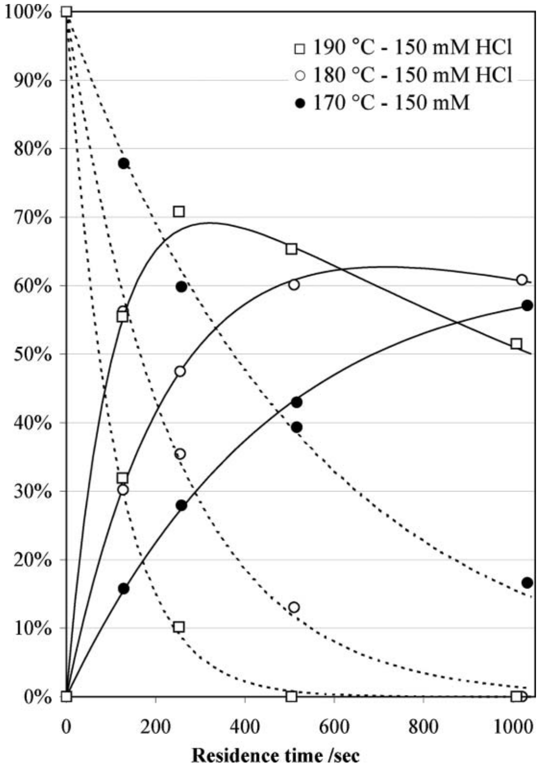

Fig. 2 Effect of temperature on xylose conversion and maximum furfural yield in 150 mM HCl. Xylose (dotted line) and furfural concentration (solid line) as from eqn (2) after fitting to the experimental results.

Taking all these results into account it can rather be postulated that the ionic species in solution other than H^+ induce a change in the reaction mechanism, and Cl^- ions seem to be the main responsible for this effect.

Different salts, namely KCl, NaCl, $CaCl_2$ and $FeCl_3$, were also tested in 50 mM aqueous HCl, keeping a constant Cl^- molarity in every solution. Results showed very similar reaction behavior for the three salts KCl, NaCl and $CaCl_2$, both in terms of xylose reaction rate and furfural yield. For these three salts the concentration of Cl^- in solution seems to be the main feature for the kinetics of xylose reaction, the different cations seemingly playing only a minor role, see Fig. 3.

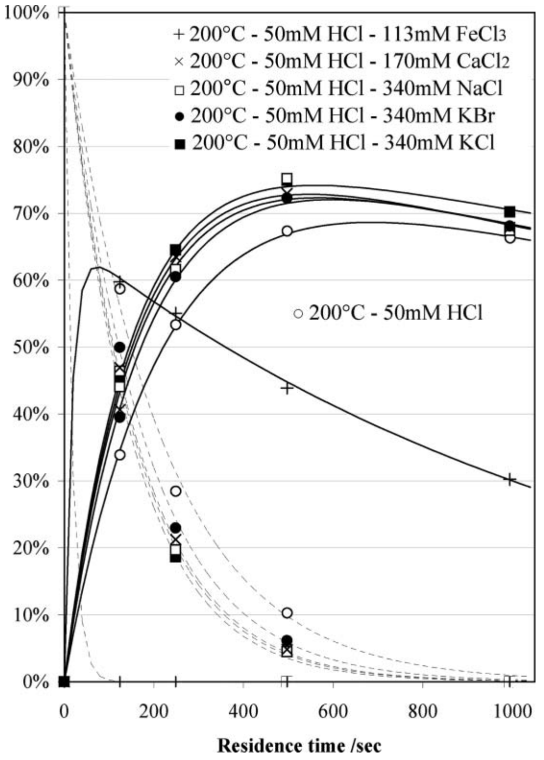

Fig. 3 Effect of different chloride salts on xylose conversion and furfural yield. Xylose (dotted line) and furfural concentration (solid line) as from eqn (2) after fitting to the experimental results.

A significantly different behavior was observed when adding $FeCl_3$, where the xylose reacted so fast that no sugar could be detected already after a residence time of 124 s, thus, even if the exact value could not be derived, the reaction rate appeared to be more than 10 times larger than in the other cases. Hence the Fe^{3+} ion itself can be considered to have a relevant catalytic effect on the reaction of xylose. On the other hand, furfural maximum yield was lower when adding $FeCl_3$ compared to the other cases, which accounted for 62% of the initial xylose, in agreement with what was shown earlier when treating corn stover under very similar conditions.[7]

The addition of electrolytes to the water can generally induce significant changes by attracting or orienting its molecules, or change its ordered short range structure and in general its interaction with the solute. Similar effects are responsible for the vapor pressure increase of aqueous electrolytes solutions, for salting-out or salting-in effects,[18] or colloids precipitation as first studied by Franz Hofmeister more than a hundred years ago.[19] In the same way these effects could be regarded as responsible for the reported results in terms of xylose reaction rates and furfural yield. Nevertheless, such effects, especially considering dilute solutions, are normally not so dependent on the nature of the electrolytes but rather on the total ion concentration, whereas, by carefully considering the results shown in Fig. 1, 2 and 3, it becomes evident that the nature of the ions is very important even in very dilute solutions. Furthermore when comparing the results for $CaCl_2$ with those for KCl and NaCl we can notice that, even if the total ions concentration in solution is 25% lower in the first case if compared to the other two, the results are very similar to each other. Thus a direct contribution of the ions to the chemistry of the reaction, rather than a change of the solvent-reactant interactions, can be considered to play the major role.

Xylose reaction in two equimolar solutions of KCl and KBr was also studied at the same conditions of temperature and acidity, see Fig. 3. The reaction rate was about 15% slower in KBr with respect to KCl, even though faster than in the absence of any added salt, while the furfural maximum yield was comparable in both cases, see also Table 1. This last result denotes the addition of metal halides in general to aqueous acidic solutions to potentially have surprisingly beneficial effect in terms of xylose conversion into furfural, with Cl^- showing to be somewhat more effective than Br^-. The reasons for this difference could include the nucleophilicity of the ions, as well as their size and charge dispersion. Nevertheless the results presented here are not enough to draw a clear conclusion. In this sense further work is needed which could unequivocally clarify the effects brought about when different ions of the series I, Br, Cl and F are present in solution.

Reaction rate of D-xylose to furfural

Different reaction kinetic mechanisms leading from xylose to furfural have been proposed in literature, from simple ones to more complicated,[1,2,20,21,22,23] but almost all of them can be expressed in a simplified way, as depicted in Fig. 5. As such a simple reaction scheme accurately fits the experimental results,

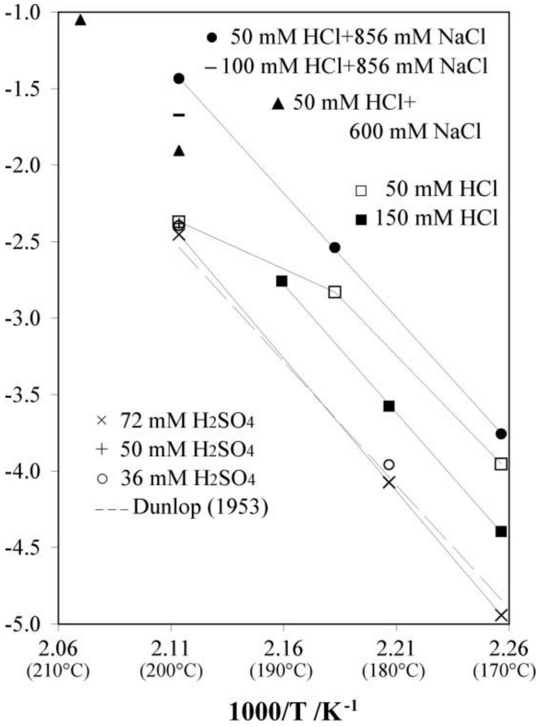

Fig. 4 $ln(k_X/[H^+])$ plot against temperature.

Table 1 Condensed results from kinetic experiments

Entry	Acid	Acid/ mM	Salt	Salt/ wt%	Total [Cl⁻]/ mM	Temp./°C	$k_X/10^{-4}[s^{-1}]$	$k_1/10^{-4}[s^{-1}]$	$k_2/10^{-4}[s^{-1}]$	$k_3/10^{-4}[s^{-1}]$	Selectivity[a] [%]	Maximum Yield[b] [%]
1	HCl	150	—	—	150	170	18.5	13.68	4.83	1.5	73.9	59.2
2	HCl	150	—	—	150	180	42.0	31.5	10.5	2.5	75.0	62.7
3	HCl	150	—	—	150	190	95.0	77.9	17.1	5.3	82.0	69.1
4	H_2SO_4	50	—	—	—	200	46.2	32.6	13.6	2.0	70.6	61.4
5	HCl	50	—	—	50	200	46.7	37.3	9.4	2.2	79.9	68.7
6	HCl	50	KCl	2.5	390	200	67.3	54.9	12.4	1.7	81.6	74.1
7	HCl	50	NaCl	2.0	390	200	64.5	52.84	11.7	2.2	81.9	72.8
8	HCl	50	KBr	4.1	390[c]	200	57.0	46.7	10.3	2.2	82.0	72.0
9	HCl	50	$CaCl_2$	2.5[d]	390	200	63.0	51.0	12.0	2.0	81.0	72.3
10	HCl	50	$FeCl_3$	3.1[e]	390	200	>600	>400	>200	8.0	65.7	62.0
11	HCl	50	NaCl	3.5	650	200	74.4	63.1	11.3	2.2	84.8	76.1
12	H_2SO_4	50	NaCl	3.5	600	200	78.7	65.1	13.6	2.0	82.7	75.3
13	HCl	50	NaCl	3.5	390	210	175.0	144.4	30.6	4.0	82.5	75.5
14	HCl	50	NaCl	5.0	906	200	119.1	107.4	11.6	3.4	90.2	81.3
15	HCl	50	NaCl	10.0	1762	200	196.8	159.4	37.4	4.3	81.0	74.4
16	Formic Acid	220	NaCl	10.0	1712	200	66.5	42.2	24.3	0.2	63.5	62.1
17	HCl	50	NaCl	5.0	906	170	11.7	9.1	2.6	0.6	77.7	65.7
18	HCl	50	NaCl	5.0	906	185	39.5	32.4	7.0	1.1	82.2	74.3
19	HCl	50	—	—	50	170	9.6	7.1	2.4	0.4	74.5	65.6
20	HCl	50	—	—	50	185	29.5	21.0	8.5	0.9	71.2	63.7
21	HCl	100	NaCl	5.0	956	200	184.1	161.4	22.7	5.1	87.7	79.2

[a] Calculated as k_1/k_X. [b] Maximum furfural yield calculated from (3). [c] Considered as [Cl⁻] + [Br⁻]. [d] $CaCl_2$ dihydrate. [e] $FeCl_3$ hexahydrate.

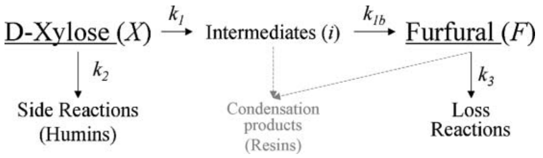

Fig. 5 D-Xylose simplified scheme of reaction.

it can by used to describe the reaction. As the initial sugar concentration is kept constant for every experiment, and rather low (35 mM), second order reactions between furfural and intermediates can be ruled out; the effect of increasing initial sugar concentration is presently being studied and it will be discussed elsewhere. Such approximation allows for describing the reaction rates by a relatively simple analytical expression:

$$\begin{cases} r_{D-Xylose} = \frac{dC_X}{dt} = -(k_1 + k_2)C_X \\ r_{Intermediate} = \frac{dC_i}{dt} = k_1 C_X - k_{1b} C_i \\ r_{Furfural} = \frac{dC_F}{dt} = k_{1b} C_i - k_3 C_F \end{cases} \tag{1}$$

Reaction intermediate(s) have never been clearly identified in literature, nevertheless, judging from experimental results, their concentration can be assumed to be low and not varying significantly with time. Hence the steady-state approximation can be introduced for the intermediate resulting in $dC_i/dt = k_1 C_X - k_{1b} C_i \cong 0$ and then $dC_F/dt \cong k_1 C_X - k_3 C_F$. Introducing this assumption makes the integration easier and the concentration of xylose and furfural can be written as:

$$\begin{cases} C_X(t) = C_{X_0} e^{-(k_1+k_2)t} \\ C_F(t) = C_{X_0} \left(\frac{k_1}{k_3 - k_1 - k_2}\right) \left(e^{-(k_1+k_2)t} - e^{-k_3 t}\right) \end{cases} \tag{2}$$

where the initial furfural concentration $C_{F_0} = 0$ and C_{X_0} is the initial xylose concentration. The maximum molar yield of furfural can also be analytically derived as a function of the three main kinetic parameters as:

$$\frac{C_{F\,\max}}{C_{X_0}} = \frac{k_1}{k_1 + k_2} \left[\left(\frac{k_1 + k_2}{k_3} \right)^{\frac{k_3}{k_3 - k_1 - k_2}} \right] \tag{3}$$

The eqn (2) were fitted to the experimental results deriving the kinetic parameters k_1,k_2,k_3 by least square minimization. The model showed very good agreement with the experimental measurements, and the results are displayed in Table 1.

The three kinetic parameters show a similar dependence on acid concentration, as it was also noticed earlier,[17] thus no significant improvements in terms of maximum furfural yield can be achieved increasing acid concentration within the range of interest for this work. Contrary to this, as it can be noticed from Table 1, chloride salts generally tend to have a direct influence on the first kinetic parameter k_1 being much less important for the others, leading to an increase of both xylose reaction rate and furfural maximum yield C_{Fmax}/C_{X_0}. From these results it is clear that a new reaction mechanism for xylose dehydration, different from the simple acid catalysed one, is followed in the presence of chloride salts.

Mechanism of furfural formation from pentoses

Contradictory theories exist in literature concerning the mechanism of furfural formation from pentoses. On the one hand, many authors consider the reaction to proceed *via* the acyclic form of the pentoses, first through a 1,2-enediol formation and subsequent three dehydration steps yielding furfural.[24,25] On the other hand, other authors believe the reaction to take place starting from the pyranose form of the pentoses,[22] which recently was postulated to take place by the action of H⁺ on a specific position of the pyranose ring, leading to a first dehydration and structure rearrangement yielding the furanose ring and subsequent dehydration to furfural.[20,26] It has been demonstrated that after reacting xylose-1-^{14}C in 12% aqueous HCl the "aldehydic" carbon of the pentose at C-1 position was found nearly completely at the aldehyde group of the final product, 2-furaldehyde-α-^{14}C.[27] Such result is perfectly aligned with the former theory, whereas it cannot be explained according to the mechanism proposed in the latter. Furthermore, in analogy to the reaction of xylose to furfural, an isomerization reaction of the D-glucose to D-fructose has been shown to take place in acidic conditions at high temperature, proving this to be the first step in the reaction leading from D-glucose to 5-hydroxymethyl furfural (HMF).[28] Besides, ketopentoses, which present a significantly higher proportion of acyclic form in water solution if compared to aldopentoses,[29,30] react much faster in water yielding furfural proportionally to the acidity of the solution.[24] From all these evidences provided by different authors throughout the years, the former theory appears to be strongly supported, whereas the latter fails to comply with some of the earlier works. For these reasons, in this work, the authors accept the first theory.

A strong indication was also provided for the 1,2-enediol intermediate to be irreversibly formed from the aldopentoses in acidic conditions, showing on the other hand a partial equilibration with the keto form.[24] Such indication is in agreement with the general aldoses reluctance to isomerization in acidic conditions,[28] and thus, since enolization reactions are normally reversible, the 1,2-enediol formation from xylose in acidic conditions can be considered to be the rate limiting step in the formation of furfural. In accordance with this, HMF is known to be formed much faster from fructose than from glucose in acidic conditions, and fructose has often been measured in the reaction from glucose to HMF, indicating aldose isomerization takes place as an intermediate step.[28,31]

Effect of the Cl^- ion on furfural kinetics of formation

Based on the results obtained in this work, it seems reasonable to postulate that one particular step among the multi-step reaction from xylose to furfural to be catalysed by both H^+ and Cl^-, this particular step being the formation of the 1,2-enediol intermediate. Thus the mechanism depicted in Fig. 6 can be drawn, which appears to be in agreement with the results obtained in this work and with what was observed in previous works. In such mechanism the presence of Cl^- favors the formation of the 1,2-enediol **2**, which can equilibrate with both the aldo **1** and keto **3** form of the sugar, and reacts to form furfural **4** in presence of an acid.

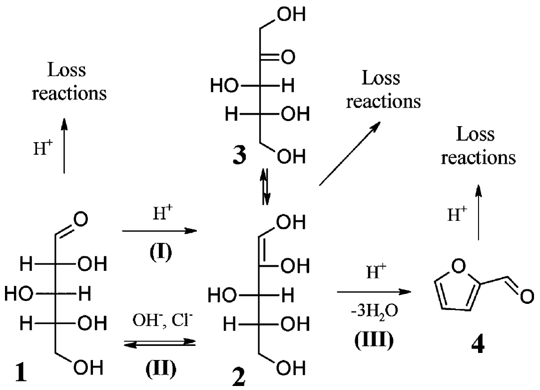

Fig. 6 Mechanism of furfural formation from xylose.

Accordingly, it is evident from the experimental results that, with increasing chloride salts concentration, xylose reacts significantly faster to furfural, while no significant effect is observed on the side reactions, resulting in a remarkable selectivity improvement. When the salt concentration becomes higher than a certain threshold with respect to the H^+ molar concentration [H^+], the increasing selectivity trend to furfural is inverted and a small drop is observed, see Fig. 1. This can be due to the larger concentration of the intermediate(s) which are prone to undergo loss reactions, including possible condensation reactions with furfural. In the simplified kinetic model proposed here this effect results in an increase of k_2, as it is observed for 10 wt% NaCl, see Table 1 entry 15. As mentioned before, **2** and **3** are more reactive than **1**, also in absence of acids,[24,31] yielding furfural proportionally to the acidity. Accordingly, the faster xylose reaction and the poor furfural yields obtained using a weak acid in presence of 10 wt% NaCl (Table 1, entry 16) can be explained due to the relatively high pH in presence of a relatively large concentration of chloride salts. In addition, comparing the results when using different strong acids like HCl and H_2SO_4 led to different results as discussed before (Fig. 1), whereas in the same conditions, when a larger concentration of chloride salt is also present, results are very similar (Table 1; entries 11–12), meaning the H^+ source does not significantly influence the reaction when a larger concentration of Cl^- is also present.

Hence, even if the reaction of xylose can be catalyzed by chloride salts by favoring the 1,2-enediol formation, the presence of a strong acid is necessary in order to favor the selectivity to furfural. This conclusion is in agreement with what was previously shown for ketopentoses, where higher acidity influenced the selectivity to furfural not influencing so much the sugars rate of reaction.[24]

The mechanism in Fig. 6 helps also to explain the Arrhenius plot depicted in Fig. 4. In this plot the natural logarithm of the total xylose reaction rate kinetic parameter $k_X = k_1 + k_2$ divided by [H^+] was plotted against the inverse of the temperature, in order to show the rate of reaction of xylose excluding the effect of acid concentration.

The bottom line in Fig. 4 shows the H_2SO_4 catalysed reaction, *i.e.* the well known H^+ catalyzed route, where formation of **2** through reaction (I) is the rate limiting step, Fig. 6. The linear relationship between k_X and [H^+] can clearly be observed, accordingly the points for different H_2SO_4 concentrations are condensed on one straight line in Fig. 4. These results are also in very good agreement with the known kinetics provided in a previous work[2] for the same range of acid concentration and temperature.

When a relatively large Cl^- concentration is present, $k_X/[H^+]$ values are larger, and accordingly they shift to higher values on the Arrhenius plot in Fig. 4. Such shift can be explained with a switch in the rate limiting step, namely from reaction (I), which is bypassed due to the Cl^- catalyzed formation of **2**, to the subsequent H^+ catalyzed dehydration reaction (III). The 50 mM HCl curved line is particularly revealing the transition: at the higher temperatures it tends to the H^+ catalysed mechanism (I);

lowering the temperature the Cl^- catalyzed reaction (II) becomes faster, having seemingly a lower activation energy, leading to a switch to reaction (III) becoming therefore limiting step.

When reaction (III) is the rate limiting step, the kinetic parameter k_X should be directly proportional to $[H^+]$, as previously shown, and indirectly to $[Cl^-]$ through **2** formation. Contrary to this, no linearity is evident between k_X and $[Cl^-]$ or $[H^+]$, the data showing a marked less than proportional relationship. It can be analytically demonstrated, and it is also qualitatively intuitive, that such relationship indicates reaction (II) to be reversible, contrary to (I), being the equilibrium between **1** and **2** only partly attained. This means that the rates of reaction (II) and (III) are comparable, thus concentration of **2** varies accordingly. Due to this, an increased acidity at fixed $[Cl^-]$ would cause reaction (III) to be faster, at the same time lowering to some extent the mean concentration of **2**, and resulting in a less than proportional observed increase of xylose reaction rate. In the same way, an increase of $[Cl^-]$ at fixed $[H^+]$ would tend to increase the average concentration of **2**, resulting again in only a less than proportional observed increase of furfural rate of formation because of the combined effect of reaction (III) and (II). In this way the 150mM HCl straight line intermediate position in Fig. 4 can also be explained.

For these conditions the competing side reactions also become more complex, involving **1**, **2** and possibly **3**, very reactive ketopentoses at lower acid concentrations as mentioned before.

The peculiar Cl^- behavior in this reaction is particularly interesting by itself. As it has been shown, there is good reason to believe Cl^- ions to act as a catalyst in the enolization reaction of xylose, which is normally catalyzed in basic environment even at lower temperatures. Alternatively the Cl^- ions could be considered to favor the presence of the 1,2-enediol with respect to both the aldose and ketose by a stabilizing effect, thus favoring the subsequent dehydration reactions starting from such form. Anyway, based on the results presented in this work, the 1,2-enediol promoting effect induced by the Cl^- remains an hypothesis consistent with the reaction kinetics of xylose to furfural, although no ultimate evidence is provided in support of this theory. This hypothesis, as well as a more general extension to other halides like I, Br and F, is to be verified with further investigation.

As far as the peculiar effect of $FeCl_3$ is concerned, not enough data are available to point out how Fe^{3+} could enter the mechanism proposed in Fig. 6. From the data available, and considering the acidic character of Fe^{3+}, it can be assumed to catalyze reaction (I) or (III) in a similar fashion like H^+ but much more vigorously, although a different mechanism cannot be excluded. In terms of selectivity to furfural the data here reported are also not deviating very much from the specific H^+ catalyzed reaction, being just moderately lower. The catalytic strength of Fe^{3+} in water, or its hydrated forms, is indeed of great interest and worth more investigation in the future.

Contrary to the dehydration reactions yielding furfural from pentoses and HMF from hexoses, which require strong acids, aldoses isomerization is normally favored by basic conditions,[28,31] and proved to proceed via the 1,2-enediol formation.[32] Moreover, in the past, it was also observed that furfural formation from pentoses was not a simple dehydration reaction, since only poor furfural yields were obtained when xylose was reacted with dehydrating catalysts like pure $ZnCl_2$ or phosphorous pentoxide, whereas, when an aqueous solution of $ZnCl_2$ was employed, furfural yield approached that obtained using strong acids solutions.[33] Thus a discrepancy in terms of "catalytic requirements" becomes evident in the process of furfural formation from pentoses, presenting in turn an enolization followed by three dehydration reactions, being the two reactions normally favored by different catalysts.

Thus, when thinking about industrial furfural production, it should be kept in mind that the high severity normally required in terms of acid concentration and temperature is mainly needed to overcome the first enolization step as it is normally not favored by acid, while acid is indeed needed for the following dehydration steps. Thus, in order to achieve better furfural yields at milder conditions and in a more environmental friendly manner, the combination of two different catalysts, having in turn basic and acidic character, would probably be the key. A recent remarkable work[34] is based on a similar observation where the combined use of acid and basic solid catalysts in a one-pot reaction allowed for exceptional HMF yields from both glucose and fructose under relatively mild conditions.

In the present work it has been shown that such double catalytic effect can seemingly be achieved by the addition of metal chlorides to aqueous acidic solutions, allowing for high furfural yields and relatively high xylose reaction rates. In terms of furfural yield maximization an optimum for H^+ and Cl^- concentrations exists, also in relation with the loss reactions, involving a relatively large Cl^- excess and a relatively low acid concentration. Noteworthy seawater typical composition with the addition of a small amount of strong acid could be a suitable solvent for furfural production.

Conclusions

Chloride salts were shown to enhance the reaction of xylose to furfural in aqueous acidic solution at temperatures between 170 and 200 °C. Experimental results indicated that the Cl^- ions promote the formation of the 1,2-enediol from the acyclic form of the aldose, which undergoes subsequent acid catalyzed dehydration reactions to furfural.

The effect caused by the chloride salts addition to aqueous acid solutions was studied under various conditions. Significant improvements were observed with respect to the H_2SO_4 -based case, furfural yield and selectivity respectively increasing by 18% and 28%, selectivity in particular attaining 90%. At the same time a 4-fold xylose reaction rate increase was possible by 1.7 M NaCl addition keeping the acid concentration as low as 50mM (0.18 wt% HCl).

Among the salts tested $FeCl_3$ showed very interesting preliminary results, producing exceptionally high xylose reaction rates. Such result can be explained by the combined effect of the Cl^- ions and the acidic character of the Fe^{3+}, even though more investigation is needed in order to clarify this aspect.

Experimental

The experimental setup consists of a coiled tube reactor immersed in a thermostatic oil bath. The reactor is made of titanium grade 2 (Merinox, Alblasserdam, NL) to ensure high resistance to corrosion and minimal catalytic effects. The tube reactor has an external diameter of 3.2 mm, internal diameter of 1.7 mm, and a length of 4.40 m. The reactants are fed to the reactor by an HPLC pump, while the reaction temperature is precisely controlled and kept constant by the thermostatic oil bath. The reactants solution enters the reactor at the set pressure and is rapidly brought to the desired temperature by means of an electrical pre-heater situated upstream the oil bath. The pre-heater consists of an aluminium block, thermally insulated from the environment, which encloses the tube reactor for a length of approximately 15 cm and is equipped with an electrical heating module and relative electronic control. Downstream the reactor is a cooling double pipe heat exchanger fed with tap water, a filter and a back pressure regulator. The reaction products are collected and analyzed as such. Reaction pressure is set at 60 bar, significantly larger than the water vapor pressure at the set temperatures, to ensure complete liquid operation. Such reactor resembles with very good approximation an ideal plug flow reactor and it allows liquid phase reaction kinetics studies to be performed under conditions up to 250 °C and 250 bar and to precisely control residence times between 100 to 5000 s. A thorough description of the reactor and its main characteristics is available elsewhere.[35]

Materials and methods

Xylose reagent grade (Sigma-Aldrich, ≥99%) was used as model compound in the experiments, and for HPLC calibration. Furfural reagent grade (Sigma-Aldrich, 99%) was used for HPLC calibration after distillation under reduced pressure (50 mbar) for further purification. Pure formic acid, HCl $40\%_{wt}$ water solution, $H_2SO_4 \geq 97.5\%$ and all inorganic salts (NaCl, KCl, $CaCl_2{\cdot}2H_2O$, $FeCl_3{\cdot}6H_2O$) were purchased from Sigma-Aldrich. The acid concentration varied between 50 and 100 mM, except for formic acid which concentration was 220 mM. Xylose concentration for every experiment was 35 mM. Acidic aqueous solutions of xylose were prepared with different amounts of inorganic salts, and fed to the tube reactor after stirring to ensure a complete dissolution of the solids.

HPLC analysis

Analysis of the reaction products was carried out by means of an HPLC apparatus equipped with a Resex ROA-Organic acid column, 8% cross linked H^+, 300 × 7.80 mm, (Phenomenex Inc., Torrance, CA, USA). A Marathon XT auto-sampler (Separations, Ambacht, NL) was used to enhance reproducibility. Xylose was quantified by means of a Refractive Index detector (Varian Model 350), whereas for furfural both Refractive Index detector and UV detector (Varian Model 310 Pro Star) were used. 10 mM sulfuric acid solution in demineralized water was used as the eluent at a flow rate of 0.8 mL min^{-1} with a column temperature of 80 °C and a run time of 33 min.

Experimental data processing

Experimental results were fitted to eqn (2) and the kinetic parameters k_1, k_2, k_3 derived by least square minimization using the Solver tool embedded in the commercial software Microsoft Excel^{TM} (2003). Selectivity to furfural and yield could also be analytically derived from (2), being selectivity $S = (k_1/k_1 + k_2)$ and furfural yield expressed as from eqn (3).

List of abbreviations

HMF	5-hydroxymethyl Furfural
wt	Weight
pK_{a_2}	Second acid dissociation constant
I	Ionic strength
z	Ion charge
γ	Ions activity coefficient
$[H^+]$, $[Cl^-]$	H^+, Cl^- molarity [mol/litre]
mM	millimolar [mmol/litre]
M	molarity [mol/litre]
HPLC	High Performance Liquid Chromatography

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